Placement of conjugated oligomers in an alkanethiol matrix by scanned probe microscope lithography

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We report the *in situ* replacement of conjugated molecules in an insulating matrix by scanned probe microscope lithography. High yield, programmable patterning of a self-assembled monolayer of dodecanethiol was performed by applying voltage pulses from a scanning tunneling microscope. Conjugated oligomers were observed to be subsequently chemisorbed onto the patterned sites. © *1999 American Institute of Physics.* [S0003-6951(99)01031-1]

Scanned probe microscopy offers a method for manipulating and modifying materials at the atomic level.[1–3] Preliminary work has been done utilizing self-assembled monolayers (SAMs) as a substrate.[4–9] In this letter, we demonstrate reproducible *in situ* scanning tunneling microscope (STM) lithographic SAM patterning and subsequent replacement of conjugated molecules in an insulating matrix at selectively patterned locations. A schematic of the process is shown in Fig. 1.

The initial substrate is a gold surface with an adsorbed SAM. An annealed Au/Cr (250 nm/50 nm) film on glass exhibited a Au(111) surface with terraces of up to several hundred nanometers with herringbone reconstruction.[10] A dodecanethiol SAM was deposited from solution at room temperature.[11] Subsequent mounting in a Teflon liquid cell of an ambient STM chamber allowed for immersion in 1,4-dioxane (Aldrich) solvent for the replacement experiments.

A Park Scientific [Universal SA1] tube-scanning ambient STM was used for both imaging and lithographic patterning. Tips were prepared from Pt/Ir (70%/30%) wires and then coated with epoxy leaving the end exposed.[12] Images were taken in constant current mode with 1.5 V tip bias (V_b) and approximately 15 pA set-point tunneling current (I_t).

To perform lithography, we applied square voltage pulses to the SAM substrate with pulse amplitude (V_p) varying from 1.8 to 3.6 V and pulse duration (T_p) from 0.5 μs to 0.5 s. A constant dc bias voltage (V_b) of 0.1 V was kept on the STM tip during the voltage pulses. A larger time constant (relative to the pulse width) in the feedback electronics is used to both maintain the tip at a constant height and avoid tip crashing. Figure 2 is an image of a sample after three consecutive voltage pulses with V_p of 3.0 V and T_p of 0.5 s. The tip was biased at V_b of 0.1 V with I_t of 0.5 nA. To have a better view of the profile of the patterned structures (pits), we invert the image by plotting the depth of the pits as positive z. The diameters and depths of the patterned structures are approximately 10 and 1.4 nm, respectively. The pit depth

is the length of dodecanethiol SAM to within the measurement resolution of the STM system. A lithographic positioning program was used to move the tip to obtain these distinct, spatially separated patterns.

We have studied the patterning yield of this STM lithography as a function of pulse voltage and pulse width (Fig. 3). The yield was defined as the percent of successful patterned structures (out of 50 pulses). Under appropriate pulse conditions patterns were produced with over 90% yield when positive pulses (sample positive with respect to the tip) were applied. There is an apparent threshold voltage for pattern formation [Fig. 3(a)].[7] Greater tip sample distance required higher threshold voltage. At pulse voltages above 3.4 V pits deeper than 1.4 nm were produced, suggesting that some of the underlying gold was removed. Pulse duration [Fig. 3(b)] was varied at various pulse voltages for fixed tip-sample separation. Reproducible patterns were created at pulse widths greater than about 0.1 s. We used positive pulses to remove the SAM in this work since we observed that negative pulses created mounds,[6–8] which may be the result of material deposition from the tip.[13]
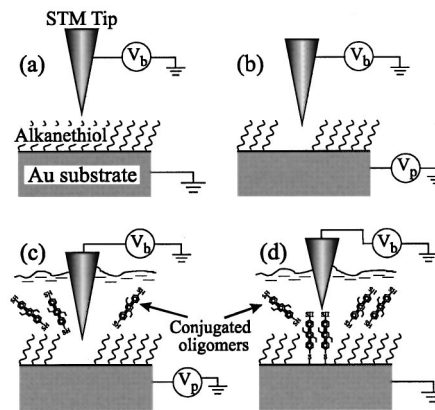

FIG. 1. Schematic of the lithographic patterning and replacement of conjugated molecules in an alkanethiol matrix: (a) normal STM imaging of the SAM surface with tip bias V_b; (b) SAM removal by applying a pulse V_p to the substrate; (c) the same as (b) in solution; (d) insertion of conjugated molecules on the patterned site.

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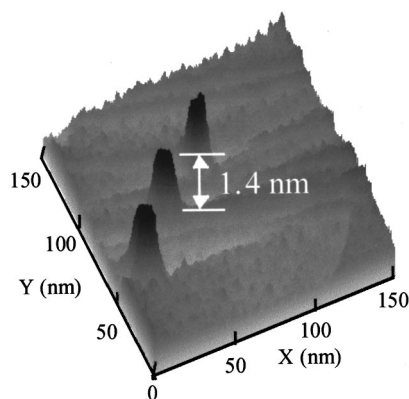| 16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
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FIG. 2. Inverted image of localized dodecanethiol SAM removal. Each pit is formed by applying a V_p of 3 V, T_p of 0.5 s voltage pulse (at V_b of 0.1 V, I_t of 0.5 nA prior to pulse and V_b of 1 V, I_t of 50 pA for subsequent imaging).
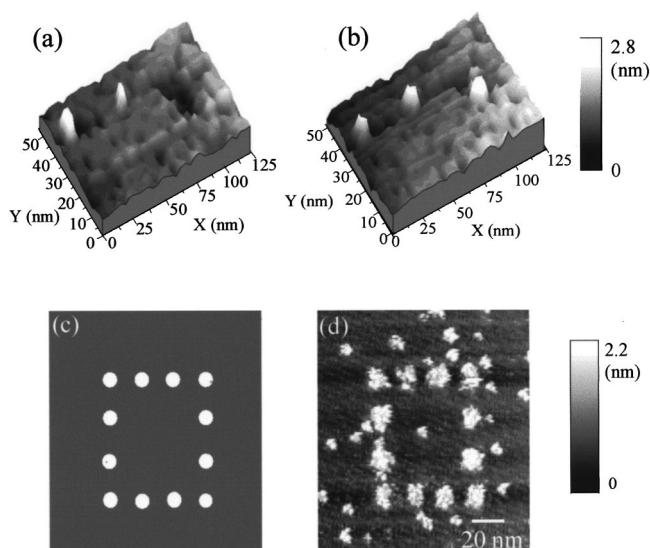

FIG. 4. (a) The image of a dodecanethiol SAM surface after consecutive pulsing at three different locations shows two peaks indicating adsorbed molecules and one pit without adsorption. (b) The image was taken a few minutes later and it shows adsorption onto the third remaining pit. (c) The programmed rectangular pattern. (d) The image of a patterned dodecanethiol SAM surface after chemisorption of molecule B showing a rectangular frame illustrated in (c). Random adsorption at unintentional defect sites is also present.

Subsequent to dodecanethiol removal, we introduced conjugated molecules into the liquid cell for ''decoration'' of the patterned sites. The conjugated molecule used is 2′-ethyl-4:1′-ethynylphenyl-4′:1″-ethynylphenyl-1,4″-thioacetylbenzene (abbreviated as A). Upon addition of NH_4OH, the protective acetyl endgroups in A are removed and cause conversion into the thiolate form (abbreviated as B), a convenient method for utilizing oxidatively unstable dithiols and which have been shown to self-assemble onto Au.[14] The mechanism for replacement adsorption is that the thiol group of the rigid rod aromatic, α,ω-dithiol binds to the exposed surface; at the concentration used (10 μM), one can estimate that there are approximately 40 collisions per second of molecules B with the exposed Au surface.

To demonstrate replacement, we added 10 μM of A in 1,4-dioxane along with several microliters of NH_4OH to the liquid cell under slightly positive Argon pressure. Lithography was performed on the dodecanethiol surface while in solution. The molecule B is similar to one previously investigated[14] in which conductivity higher than alkanethiol was observed, resulting in bright spots in the STM image. Shown in Fig. 4(a) is an STM image after three spatially

separated pulses on the SAM surface. The left of the image shows two bright peaks (indicating adsorbed molecules); the third pulsed site is a patterned pit that remained unadsorbed. Figure 4(b) is an STM image scanned minutes later showing adsorption at the third peak. The widths of the peaks are approximately 10 nm indicating the insertion of a bundle of approximately 400 B molecules. The height is about 0.7 nm above the background, which is consistent with the known length of B and dodecanthiol molecules of 2.2 and 1.4 nm, respectively.[14] Shown in Fig. 4(c) is a defined grid pattern and Fig. 4(d) an image after chemisorption of the B molecules onto the pattern (as well as random adsorption of the molecules at defect sites[4]). Several scans over one hour showed no pattern degradation.

We have demonstrated the controlled insertion of conjugated molecules in an insulating background, providing a general method for generating intermixed SAMs of arbitrary shapes and compositions. The sharpness and regularity of the STM tip should play an important role; we suggest that future work utilizing a carbon nanotube STM tip might implement single molecule replacement.
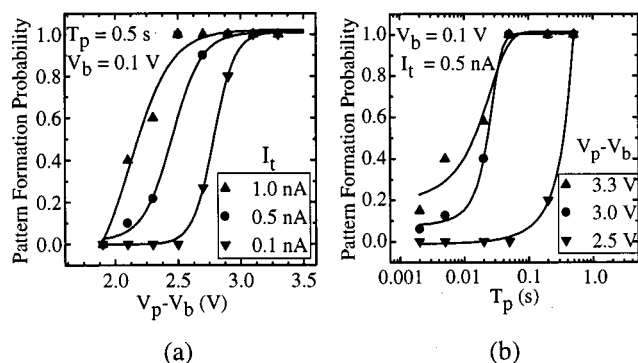
FIG. 3. (a) The probability of pattern formation of dodecanethiol on Au(111) as a function of pulse voltage amplitude between the sample and the STM tip ($V_p - V_b$) for three different I_t values with tip bias V_b of 0.1 V and a square pulse duration T_p of 0.5 s. (b) The probability of pattern formation of dodecanethiol on Au(111) as a function of T_p for various ($V_p - V_b$) values with initial tip condition: $V_b = 0.1$ V and $I_t = 0.5$ nA. In both (a) and (b), each data point represents the percent of successful patterned structures out of 50 pulses, and the data points are connected by best-fit curves.

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